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ORIGINAL PAPER

The efficacy of using electrokinetic transport in highly-contaminated offshore sediments

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Abstract Contaminated offshore mud samples from two regions of Abu Dhabi were tested for selected element removal using electrokinetics. The efficacy of the test results were compared for low and high salinity pore fluids applied to the mud samples. All samples showed some degree of removal efficiency at the anode end of each specimen by 24-h duration tests. The significance of the work was that similar removal efficiencies of about 20 ± 10% were achieved in both the low and high salinity specimens of these heavily contaminated offshore muds, revealing the potential of electrokinetic treatment in marine environments. The electroosmotic efficiency, as measured by the cumulative volume of flow per Coulombs of charge, was 0.002 cm^3/C for the low salinity and 0.006 cm^3/C for the high salinity samples. These values compared well with the electroosmotic efficiency of 0.008 cm^3/C reported for a synthetic soil reference matrix of high electrolyte content. The low electroosmotic efficiency showed that although flow was achieved in all specimens, the mass transport was mainly dominated by electromigration as expected, and not by electrosmosis.

Keywords Offshore sediments · Mass transport · Salinity · Contaminated muds · Electroosmotic efficiency · Electromigration

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1 Introduction

Direct current electrical methods are continuously tested and improved both in the laboratory and in the field for environmental restoration solutions [1, 3]. The effectiveness of the process to remove soluble metal compounds up to 99% from synthetic soil matrices have been demonstrated in the laboratory by many researchers for the last two decades. Successful but limited field applications, both in situ and ex situ have also been reported for the same duration of time. There has been little work done on the applicability of the technology to contaminated offshore muds, mainly due to predicted high energy consumption in high-salinity environments. Yet, compared to currently incurring high costs of restoration of navigation channels and sea-ports by dredging, stabilization or capping, electrokinetics may offer a feasible option to detoxify these large volumes of contaminated muds and sediments near shore. This paper addresses the first attempt undertaken at the newly-established Electrokinetic Laboratory of the Petroleum Institute in Abu Dhabi, U.A.E. to determine the efficacy of electrokinetic transport in contaminated muds of the Port of Abu Dhabi.

2 Investigation

2.1 Test and sample protocols

The apparatus used in the series of tests reported here was the Lehigh Electrokinetic (EK) Test apparatus which consisted of two parts: an EK cell and a flow control panel. The schematic diagrams of the cell and apparatus assembly are given in Fig. 1a and b. The EK cell consists of a soil container, two water reservoirs that house the electrodes on

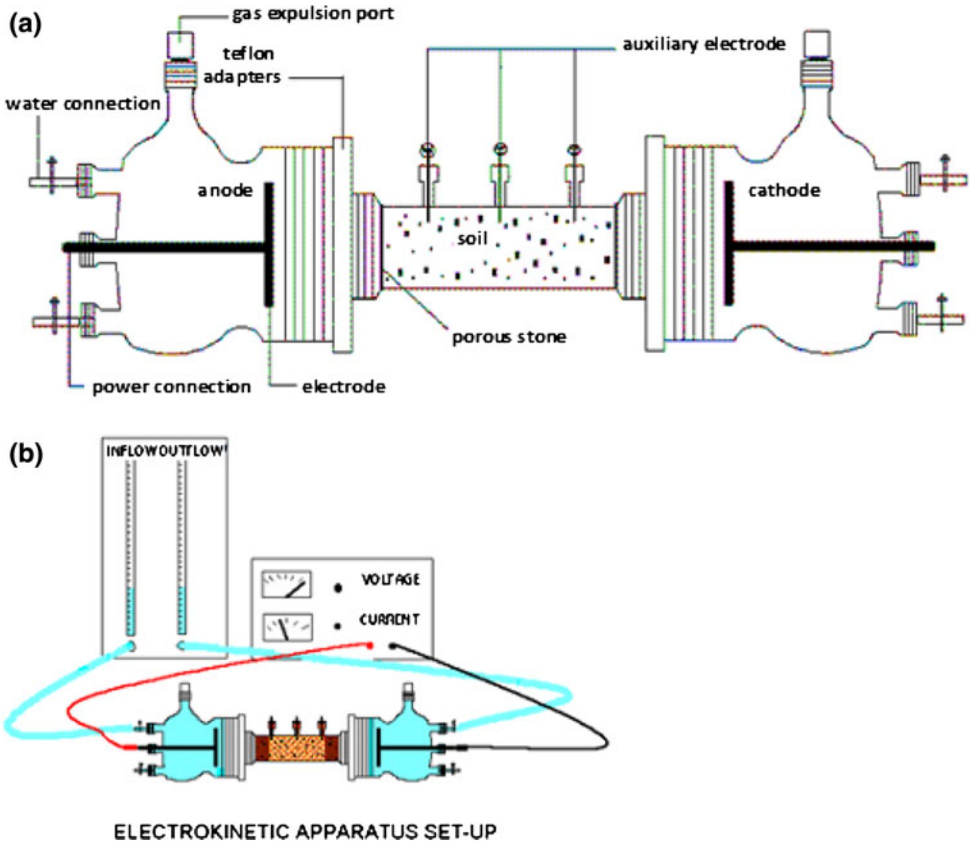

Fig. 1 **a** Schematic diagram of Lehigh electrokinetic cell, **b** typical electrokinetic apparatus assembly (after Pamukcu [3])

each side of the container. The soil container, or sample tube has an ID of 2.7 cm and a length of 10.2 cm and is made of clear glass tube with threaded ends. The electrode chambers are approximately 175 cm^3 in volume. Teflon couplers are used to attach the soil sample tube to the electrode chambers at each end. Electrode assemblies with a surface area of 22.6 cm^2 facing the soil specimen are constructed of graphite rods of 0.635 cm diameter each held together with conductive adhesive. Teflon or stainless steel quick-connections are provided on the back wall of the electrode chambers. Gas expulsion or liquid extraction/injection ports are provided on the top of each electrode chamber. Sample extractions or fluid injections are accomplished using a volumetric syringe that allows for accurate control of quantities of fluids. Graduated glass burettes with a capacity of 25 cm^3 each are used to measure inflow, normally at the anode (positive electrode) chamber, and outflow, normally at the cathode (negative electrode) chamber to an accuracy of 0.1 cm^3. The protocols of conducting EK tests using the Lehigh apparatus are described in detail elsewhere [3, 6]. Standard procedures were utilized to analyze the elements in the water and soil samples [5].

Twenty two different samples of offshore muds were collected along the coastline near Abu Dhabi, UAE from study areas designated as “Area A” and “Area B”. Area A is located along the coastline of Abu Dhabi city and Area B is 250 km away, along the coastline of Ruwais Industrial Complex near the border between Abu Dhabi Emirate and Qatar [2]. Samples from Area A were designated as *A*bu *D*habi *O*ffshore *M*uds (ADOM) and samples from Area B were designated as *R*uwais *I*ndustrial *C*omplex *O*ffshore *M*uds (RICOM). These samples were tested for a total of 35 elements. Out of the these 35 elements, 29 were present in the mud samples at varying concentrations depending on their proximity to refineries, aluminum plants, petrochemical plants, desalinization plants, and other industries. The pore fluid applied in preparation of the samples and also used to fill the electrode chambers was obtained from Abu Dhabi seashore, and is referred to as Abu Dhabi seawater in this paper. The electrolyte concentration of this water was measured at 37,000 ppm, with Na, Cl, Mg, S, K, Ca, Br as the major contributing elements.

The natural water salinity of the samples where they were collected was high, on the order of 2%, resulting in significantly high currents in all EK tests with constant 20 V applied at the electrodes. Although the voltage controlled current may be optimized to improve the removal efficiencies, while reducing both the operating cost as well as the electrode reactions that produced the O_2 and Cl_2 gases at anode and H_2 gas at cathode, this was not attempted for the basic tests conducted here. In-as-much as basic conditions are established at the cathode, there was precipitation of hydroxides and carbonates, which caused visible cementation and accumulation of transported mass near the cathode region of the soil, and in the cathode chamber as well.

All experiments were conducted under 20 V and lasted 24 h on equally consolidated offshore mud samples to a pressure of 207 kPa (30 psi). Select samples were mixed with pore water of different salinity to make 100% water saturated mud mixtures and then packed into separate consolidation cells to compact them into the desired pressure and size test specimens to use in the EK cells. The average total mass densities of the specimens were 1.94 ± 0.14 g/cm^3, and their water contents ranged from 30 to 40% at near 100% water saturation.

First, 75 samples randomly selected from the ADOM and RICOM clusters were mixed with Abu Dhabi seawater diluted to a salinity of 10 ppm (0.000010 mg/l) using distilled water. The next 30 samples, again randomly selected, were mixed with the Abu Dhabi seawater at its full strength of salinity, 37,000 ppm (0.037 mg/l). The first set of samples are referred to as the "low salinity" pore fluid specimens, while the second set are the "high salinity" pore fluid specimens. The electrode chamber fluids were selected as the 10 ppm and the 37,000 ppm seawaters for the low and high salinity specimen, respectively. Another distinction between the two sets of tests was that in the high salinity tests a weak organic acid, maleic acid at a concentration of 0.0045 mg/L was added into the electrode chambers for pH control.

The low salinity specimens exhibited current measurements in the range of 10–45 mA with a mean of 32 mA during the tests. The high salinity specimens exhibited test currents in the range of 35–85 mA, with a mean of 60 mA, all under constant 20 V DC. Evidence of chlorine gas production was observed in high salinity tests, which was not addressed in this study. The removal efficiency was calculated using Eq. 1 below. The initial concentrations were always determined at the anode region of the mud specimen and assumed to be uniformly distributed because of the initial mixing and consolidation process used to prepare the test specimens.

$$\text{Removal efficiency } (\%) = 100\,[1 - (\text{final concentration}/\text{initial concentration})] \quad (1)$$

3 Results and discussion

3.1 Low-salinity tests without pH control

Table 1 presents the removal efficiencies calculated at the anode region for various select elements in the low salinity test specimens. The average removal efficiency at the anode was 20 ± 10%. Table 1 also lists for reference the drinking water limits posed by three different world standards for the tested elements. The spatial distributions of post-EK concentration of three elements are presented in Figs. 2, 3 and 4. These elements were selected to represent three different orders of magnitudes of initial concentrations present in the specimens and they also represent relatively higher levels of contamination in the mud samples, which are unrelated to the background values found in the seawater (see Table 2 for the representative seawater values). It should be noted that no chemical balances were attempted to support these results as it was only intended to compare the results for low and high salinity condition tests in this work. The consistency of the magnitude and distribution of the removal efficiencies measured for the large number of samples tested offered an indirect confidence in the chemical results presented here.

Figure 2 shows the concentration of the arsenic found at three locations across the length of the test specimen ADOMAs4: anode end, center and cathode end after 24 h of electrokinetic treatment. Close to a linear reduction of arsenic is observed from anode to cathode region, with an average of 26% overall. Similarly, Fig. 3 shows the remaining concentration distribution of chromium at the end of 24 h of electrokinetic treatment in test specimen RICOMCrR3. Once again the removal efficiency exhibits a near linear distribution, with 11% overall. Figure 4 shows the distribution of aluminum in RICOMAlR3, which was found at significantly higher concentrations than any other element in all the mud samples (see Tables 1, 2). Again fairly linear distribution of post-EK aluminum concentration is obtained with an overall removal efficiency of 17%. The significance of the post-EK concentration distributions of these select elements of different initial concentrations is that they show little or no accumulation at the discharge end (cathode end) of the specimens. These results demonstrate that favorable conditions were achieved under the average 32 mA of current for uniform and fast removal of these and other elements as listed in Table 1. It should be noted that the low salinity tests, were conducted with no pH control, whereby the post-EK pH at the anode and cathode chambers were typically measured at around 2 and 10 pH units, respectively.

Table 1 Removal efficiencies of select elements in low salinity samples at anode location after 24-h EK test using applied pore water of 10 μg/kg (10 ppm) salinity and no pH control (the results are compared to Canadian, U.S. and WHO drinking water limits for reference)

Element	Sample ID[a]	Initial concentration (μg/kg)	Final concentration at anode (μg/kg)	Removal efficiency at anode (%)	Canadian limit (ppm)[b]	US limit (ppm)[c]	WHO limit (ppm)[d]
Aluminum	ADOMAl4	459	364	21	0.1	0.05–0.2	No limit
	ADOMAl5	265	178	33			
	RICOMAlR3	645	505	22			
Arsenic	ADOMAs4	1.28	0.84	34	0.01	0.01	0.01
	ADOMAs5	0.51	0.42	18			
	RICOMAsR3	0.45	0.41	9			
Barium	ADOMBa2	6.36	5.66	11	1	2	0.7
	ADOMBa4	3.08	2.66	14			
Beryllium	ADOMBe4	0.019	0.017	11	No limit	0.004	No limit
	ADOMBe5	0.012	0.009	25			
	RICOMBeR3	0.049	0.037	24			
Cadmium	ADOMCd2	0.015	0.010	33	0.005	0.005	0.003
	ADOMCd3	0.019	0.014	26			
	RICOMCdR3	0.014	0.012	14			
Chromium	ADOMCr5	4.99	3.97	20	0.05	0.01	0.05
	RICOMCrR3	7.65	6.52	15			
Copper	ADOMCu3	2.31	1.95	16	1	1.3	2
	ADOMCu5	0.75	0.67	11			
	RICOMCuR3	1.89	1.18	38			
Lead	ADOMPb2	2.79	2.43	13	0.01	0	0.001
	RICOMPbR3	0.67	0.47	30			
	RICOMPbR4	0.57	0.43	25			
Zinc	ADOMZn2	4.40	3.81	13	5	5	No limit
	ADOMZn3	4.98	2.78	44			
	ADOMZn5	1.33	1.23	8			

[a] ADOM(element)(sample #)—Abu Dhabi Offshore Mud(element name)(sample number): samples from 1 to 5; RICOM(element)(sample #)—Ruwais Industrial Complex Offshore Mud(element name)(sample number): samples from R1 to R4

[b] As per Canadian or BC Health Act Safe Drinking Water Regulation BC Reg 230/92, & Sch 120, 2001. Task force of the Canadian Council or Resource and Environment Ministers Guidelines for Canadian Drinking Water Quality, 1996

[c] As per the U.S. Environmental Protection Agency Drinking Water Standards

[d] As per the WHO Guidelines for drinking water quality [7]

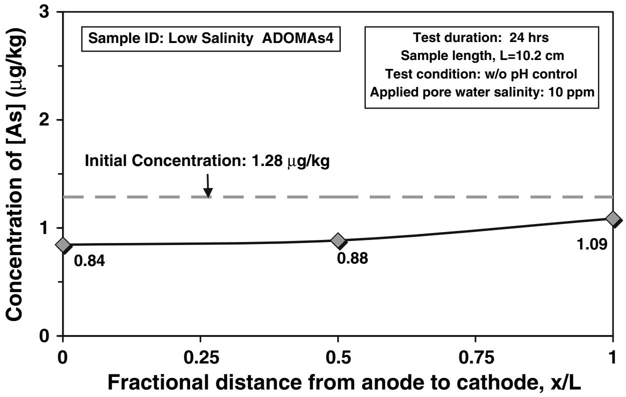

Fig. 2 Concentration profile of Arsenic (As) along sample length after 24-h EK test (Abu Dhabi Offshore Mud—ADOM)

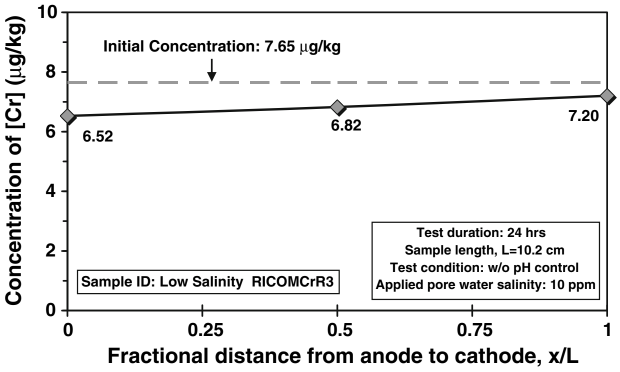

Fig. 3 Concentration profile of Chromium (Cr) along sample length after 24-h EK test (Ruwais Industrial Complex Offshore Mud—RICOM)

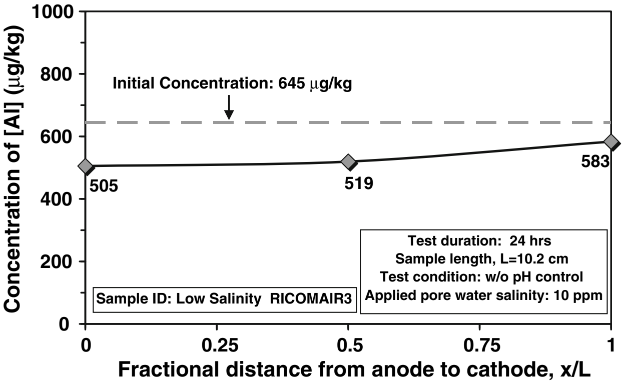

Fig. 4 Concentration profile of Aluminum (Al) along sample length after 24-h EK test (RICOM)

3.2 High-salinity tests with pH control

Table 2 shows the results of the removal efficiencies calculated for various select elements in high salinity test specimens. These tests differed from the former ones as they incorporated a weak organic acid (maleic acid at concentration of 0.0045 mg/L) added to the electrode chambers for pH control. Table 2 also lists for reference the representative seawater concentrations of the tested elements. Slightly increased removal efficiencies, on the order of 24 ± 10% were recorded in these tests overall. This increase is not contributed by the higher salinity of the pore fluid used since as shown in Table 2 the concentrations of the measured elements in the full strength seawater were insignificant compared to their respective values in the mud samples. The increase is also statistically insignificant, hence it is concluded that the high salinity environment tests resulted in similar removals as those of the low salinity environment tests.

Figures 5, 6 and 7 show the post-EK concentration distribution of three selected elements, Beryllium, Barium and Zinc. These elements showed notable difference in removal between the low salinity and high salinity

Table 2 Removal efficiencies of heavy metals in high salinity samples at anode, center and cathode locations after 24-h EK test using applied pore water of 37,000 μg/kg (37,000 ppm) salinity and pH control at the electrodes

Element	Sample ID[a]	Initial concentration (μg/kg)	Final concentration at anode (μg/kg)	Removal efficiency at (%)[b]			Seawater at 3.5% salinity (μg/l)
				Anode	Center	Cathode	
Aluminum	ADOMAl1	1570	1105	30	0	−6	
	ADOMAl2	1176	806	31	15	6	0.001
	ADOMAl3	1248	1064	15	−24	0	
Barium	RICOMBaR1	17.5	14.8	15	−21	0	
	RICOMBaR2	8.4	6.1	27	−36	0	0.021
	RICOMBaR3	8.3	5.3	36	15	−12	
Beryllium	ADOMBe1	0.1	0.08	20	1	6	
	RICOMBeR2	0.06	0.04	33	17	−6	6×10^{-7}
	ADOMBe3	0.06	0.05	17	−16	6	
Cadmium	RICOMCdR1	0.06	0.05	17	2	0	0.00011
	RICOMCdR2	0.07	0.06	14	−17	0	
Chromium	ADOMCr1	15.5	12.5	19	−5	−4	
	ADOMCr2	11.5	9.3	19	8	0	0.0002
	ADOMCr3	11.6	9.4	19	−5	11	
Copper	ADOMCu2	4.9	4.1	16	14	8	0.0009
	RICOMCuR2	4.4	3.3	25	18	17	
Gallium	ADOMGa1	1.4	1.0	29	14	0	
	ADOMGa2	0.7	0.5	29	−14	0	0.00003
	ADOMGa3	0.7	0.56	20	−17	7	
Lead	ADOMPb1	1.2	0.64	47	13	34	0.00003
Strontium	ADOMSr3	9.7	8.5	12	3	−13	8.1
Zinc	ADOMZn1	12.8	11.3	12	−2	2	
	RICOMZnR2	9.7	8.5	12	5	−4	0.005
	RICOMZnR3	20.5	9.63	53	52	47	

[a] ADOM(element)(sample #)—Abu Dhabi Offshore Mud(element name)(sample number): samples from 1 to 5; RICOM(element)(sample #)—Ruwais Industrial Complex Offshore Mud(element name)(sample number): samples from R1 to R4

[b] Those locations with accumulation take on a "negative" sign

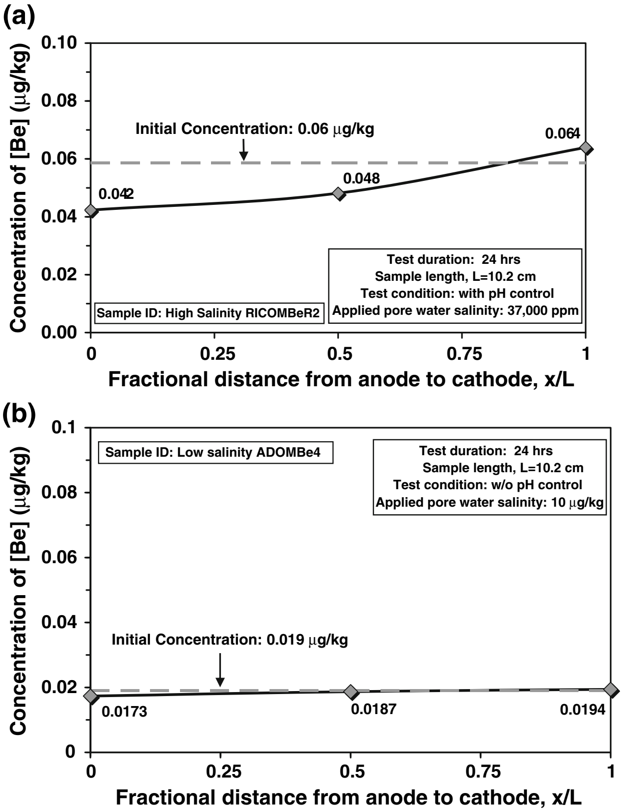

Fig. 5 **a** Concentration profile of Beryllium (Be) along sample length after 24-h EK test of high salinity environment (RICOM), **b** concentration profile of Beryllium (Be) along sample length after 24-h EK test of low salinity environment (ADOM)

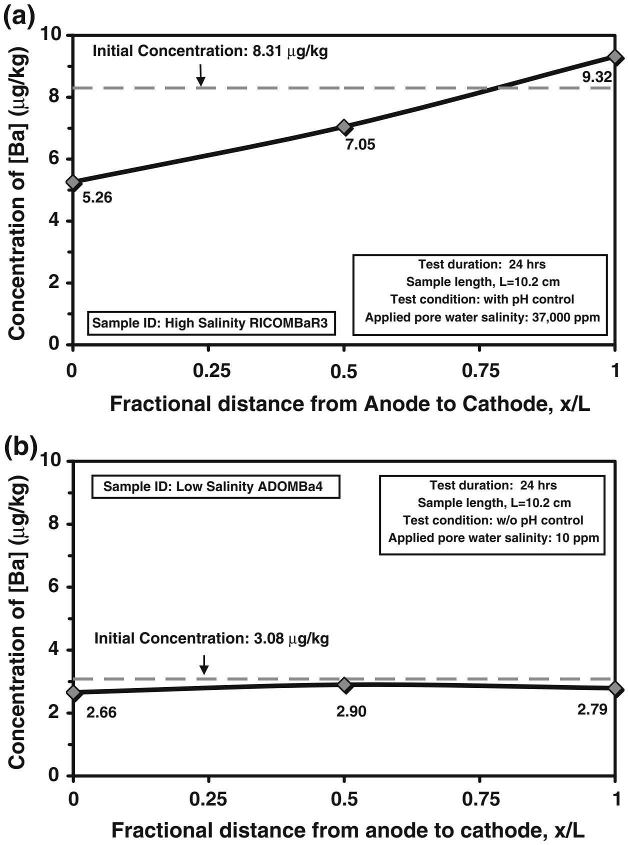

Fig. 6 **a** Concentration profile of Barium (Ba) along sample length after 24-h EK test of high salinity environment (RICOM), **b** concentration profile of Barium (Ba) along sample length after 24-h EK test of low salinity environment (ADOM)

environments. They also represented three different ranges of concentration present in the mud samples. The part "a" of each figure shows the high salinity test result, while part "b" shows the low salinity test result. In each case, the low salinity distributions show little removal across the specimen, most being at the anode end. The high salinity environment, possibly coupled with the pH control provided at the electrode chambers appear to result in better removals in all three cases. Again, fairly linear distributions of post-EK concentrations are observed for each element across the specimens. Some accumulation was observed at the cathode end for some of the elements, as exemplified with the Ba and Be distribution (also see Table 2) even in the presence of pH control. But higher removals at the anode (~30%) were recorded for most of those cases.

The significance of the comparative data and the data presented in Table 2 is that the high salinity environment did not retard the electromigration of the select elements as previously thought. The high transference numbers of the abundant ions in the seawater, such as Na, Cl, Ca, and K did not seem to interfere with the electromigration of the lower concentration elements, although as high as up to 85 mA (average of 62 mA) of current was achieved in some of these tests.

3.3 Electroosmotic efficiency

Figure 8 shows electroosmotic flow efficiency by a representative test, where cumulative volume of flow is plotted against total charge transfer in Columbs. The electroosmotic efficiency is computed as the slope of the straight line portion of the curve, given as $K_{eff} = Q/q$, where Q is the cumulative volume of flow and q is the charge. The K_{eff} factor is a practical measure of the contribution of electroosmosis and electromigration to the mass transport that occur in a soil medium under electrokinetic treatment. A higher factor signals that the mass transport is achieved predominantly by electroosmotic advection; and a lower factor signals that it is by electromigration. It has been shown previously that K_{eff} is dependent on the mineralogy of the soil medium as well as the ionic strength of the pore fluid [4, 6]. As a result, K_{eff} is inversely proportional to the ionic strength. For example, the K_{eff} factor for kaolinite clay and montmorillonite clay mixed with distilled water have been

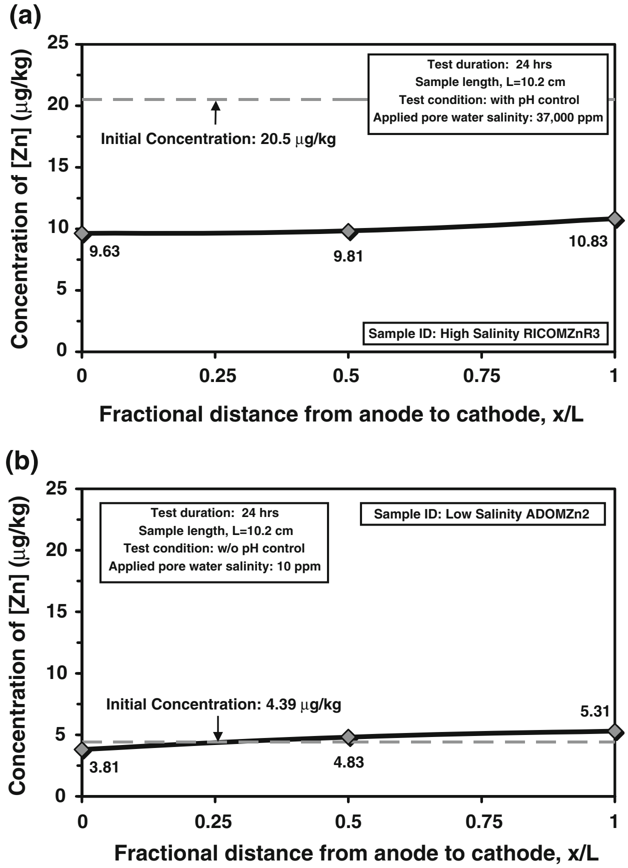

Fig. 7 **a** Concentration profile of Zinc (Zn) along sample length after 24-h EK test of high salinity environment (RICOM), **b** concentration profile of Zinc (Zn) along sample length after 24-h EK test of low salinity environment (ADOM)

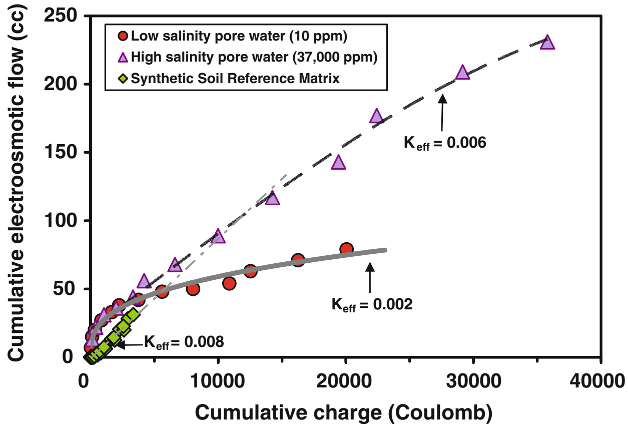

Fig. 8 Comparison of electroosmotic efficiency, K_{eff}, measured in high and low salinity specimens (K_{eff} = volume of flow per Coulombs of charge (cm^3/C))

measured as 0.14 and 0.04 cm^3/C, respectively, showing higher potential of electroosmotic flow for kaolinite than montmorillonite clay at the same charge transfer [4].

K_{eff} factors for the high salinity and the low salinity specimens in this work are computed as 0.002 and 0.006 cm^3/C, respectively, as shown in Fig. 8. Superimposed on the graph is the K_{eff} computed for a synthetic soil reference matrix (SSRM) with high ionic strength [4]. The value computed for SSRM, 0.008 cm^3/C compares well in magnitude and order to the K_{eff} of the low and high salinity specimens tested in this study. The low range of K_{eff} values clearly indicates that the mass transport is predominantly occurring by electromigration. The slightly higher K_{eff} value for the high salinity specimen may be due to the presence of the organic acid (maleic acid) in the system. The possible reactions of this acid with the resident elements in the mud samples were not evaluated, hence a conclusive statement as to its influence on the mass transport cannot be made.

The significance of the electroosmotic efficiency data is that the field mud samples tested for electrokinetic treatment conform to the expected linear relation of charge versus volume of electroosmotic flow, displaying notable volume of flow, and the measured K_{eff} factor comply well with data obtained from controlled lab tests of synthetic matrices.

4 Conclusions

Research and field works in recent years demonstrate well the effectiveness of electroremediation of contaminated soils, sludges and muds. Although electrokinetic purging has not been successful in all cases, the results of preliminary work reported here, using a sufficiently large number and variety of field retrieved samples demonstrate that the method can be recommended as a convenient and cost-effective cleaning technology for offshore muds. The results presented here show that electroremediation may be a viable solution for their in situ clean-up even in high-salinity environments. Acceptable removal efficiencies of 20% were achieved at the anode region of the field-collected offshore mud samples with 20 V DC applied over the short duration of 24 h using both low-salinity and high-salinity pore fluid conditions. The electroosmotic efficiency measured for these specimens ranged from 0.002 to 0.006 cm^3/C, which compared well with that of a similar soil. Further work will be required with longer term treatment and optimized pH control mechanisms while addressing the chlorine gas mitigation solutions.

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